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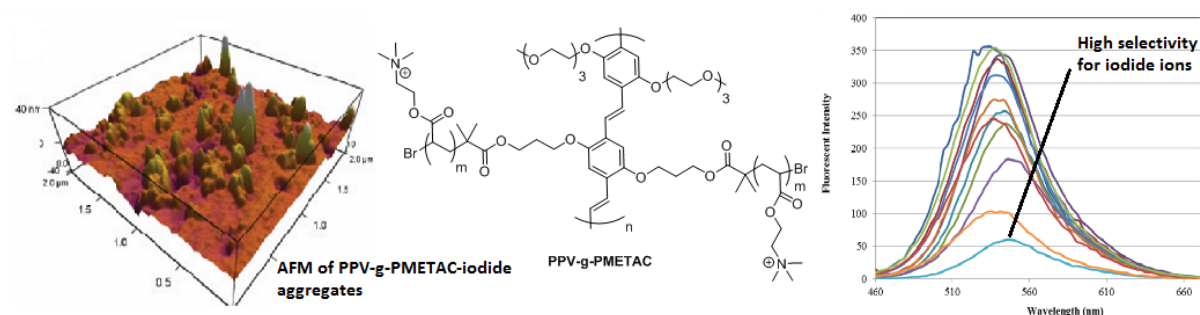
Poly-*p*-phenylenevinylene-*g*-poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride (PPV-*g*-PMETAC): a fluorescent, water-soluble, selective anion sensor

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Abstract

The photophysical and ion-sensing properties of densely grafted conjugated polymer poly-*p*-phenylenevinylene-*g*-poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride (PPV-*g*-PMETAC) are presented herein. The grafted polymer exhibits excellent iodide-sensing which is easily observed using fluorescence spectroscopy. The iodide detection limit for PPV-*g*-PMETAC was found to be 10 nM and was independent of temperature and pH less than 12. The change in fluorescence of PPV-*g*-PMETAC, upon exposure to iodide, was attributed to polymer aggregation due to changes in the morphology of the grafted PMETAC side chains, which was observed using atomic force microscopic and dynamic light scattering studies.

Keywords

PPV; graft copolymer; AFM; iodide sensor; ion sensing.

1 Introduction

Conjugated polymers (CPs) are synthetic organic materials that have garnered a wealth of recent attention owing to their potential for use in a wide range of applications in various fields, including the development of optical and electrical devices,¹⁻³ solar cells⁴⁻⁷ and usage in the engineering and modification of surfaces.^{8,9} Additionally, CPs have been investigated for their application in the biological and medical sector,¹⁰ as well as for their abilities to act as actuators and sensors.¹¹⁻¹³ Related to the latter, a number of CP sensors have been developed particularly for the detection of specific inorganic ions – such substances are beneficial in a range of biological and medical applications.¹⁴⁻¹⁷

Iodide ions are essential for a number of biological processes, including the activity of neurons and the thyroid gland. As such, the sensing of iodide ions is a field of great interest, with a number of studies focussing on the development of methods to detect these ions. Such methods and iodide sensors would have a significant potential impact and usage in the chemical and pharmaceutical industry.¹⁸⁻²⁰ To meet this need there has been previous work on the development of colourmetric and fluorometric iodide sensors.²¹⁻²⁵ These sensors have a range of sensitivities (from 10-100 nM) and are influenced by various factors including pH, where often only a narrow pH range is optimal. Selectivities of the previous sensors for iodide also vary from two-fold to greater than six-fold. Some of the best iodide sensors unfortunately require the addition of toxic mercury salts in their sensing mechanism.^{23,25}

With respect to biological and environmental sensors, water solubility is a desirable property. Water solubility has proven difficult to attain for CP-based sensors, with most approaches focussing on the structure and design of the conjugated backbone. In general, the rigid conjugated backbone has low aqueous solubility – to mediate this and improve the hydrophilicity of the CP, various chains - ionic²⁶ and non-ionic^{27,28} – have been incorporated into the structure of the backbone as pendants. Amongst the modified CP-based sensors, some of them have exhibited ion-sensing capabilities, including the ability to detect iodide.¹⁸

CPs have been shown to have much-enhanced sensing abilities over the previously-used small molecules and it has been shown that the main reason for this increased sensitivity is through a greater number of responsive sites present in CPs.^{26,29,30}

To further utilise the advantage that an increased number of responsive sites provides CPs over more traditional sensors, attentions have now turned to further amplifying the number of

responsive sites present in a CP, by grafting additional molecular brushes onto the CP.³¹⁻³³ CPs with grafted molecular brushes have received increased interest because of their increased structural efficiency and resulting high performance in sensing applications.^{34,35} Research has also shown that CP-based grafted molecular brushes undergo various conformational and structural changes in both the molecular brushes and the backbone when exposed to various different external conditions.³⁶ Separation of the responsive sites from the CP backbone, by incorporating them onto the molecular brushes has resulted in the synthesis of a new class of stimuli-responsive material.³² Such responsive and smart materials are of particular interest to a number of applied sectors, including environmental, biomedical, biological and pharmaceutical fields.

We recently reported the synthesis of highly water-soluble grafted CPs bearing poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride (PMETAC) brushes using ARGET ATRP from a CP macroinitiator.³⁷ Herein, we present our studies on the anion-sensing ability of the cationic grafted copolymer poly-*p*-phenylenevinylene-g-poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride (PPV-g-PMETAC) (Figure 1).

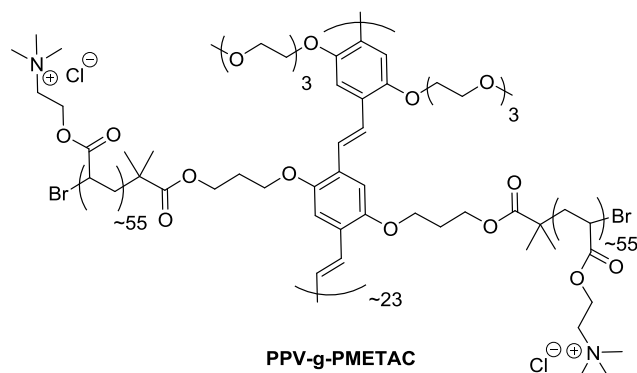


Figure 1. Structure of PPV-g-PMETAC

2 Materials and Methods

2.1 Materials

Solvents and reagents were purchased from commercial sources and used as provided. The synthesis of PPV-g-PMETAC was carried out using previously reported procedures.³⁷⁻³⁹ GPC: M_w : 22.9×10^3 , M_n : 16.7×10^3 , PDI: 1.37. Higher molecular weight samples of PPV-g-PMETAC have lower aqueous solubility and as such were unsuitable for this investigation. Solution state, in water, quantum yield of the PPV-g-PMETAC used in this study was calculated to be 0.58 [relative to Anthracene 314 in ethanol ($\phi = 0.27$)].

2.2 Spectroscopic Measurements

UV-Visible measurements were obtained using a Pharmaspec UV-1700, Shimadzu spectrophotometer. Measurements were recorded using PPV-g-PMETAC (1 mgmL⁻¹) in milli-Q water, resistivity at 25 °C filter, 18.2 Ω or Hofmeister series salt solutions (2.5-25 μM).

Fluorescence measurements were recorded with a Perkin Elmer LS 55 spectrophotometer, using a 3-Q-10 mm rectangular quartz cell. Fluorescence spectroscopy measurements were conducting using PPV-g-PMETAC (1 mgmL⁻¹ in water) which was further diluted to 25 μmL⁻¹ in the corresponding solution, to prevent polymer self-quenching. The intensity and spectral shift of $\lambda_{\text{max Em}}$ was measured using the various Hofmeister series salts, at different concentrations.

2.3 Light Scattering Measurements

Dynamic light scattering (DLS) measurements were recorded through the use of a Malvern Zetasizer photometer. Vertically polarised light was emitted from the light source with red badge at $\lambda_0 = 632.8$ nm. Cells were placed in the Malvern/DLS-5000 compact goniometer system in *cis*-decahydronaphthalene. The light was detected using S₉₀ and ZS₉₀ instruments with optics that have a 90° scattering detector angle with scattering angles between 12.8° and 175°. To compare polymer sizes, polymer (10 μL of 1 mgmL⁻¹ in water) was added to 1.5 mL of either potassium or sodium iodide solutions of varying (2.5 μM-25 μM) concentration. All experiments were performed using plastic disposable cuvettes at room temperature, adjusting the angular range from 30° and 150°.

2.4 Atomic Force Microscopy Measurements

Atomic force microscopy (AFM) was performed using an Asylum Research Cypher ES instrument (Oxford Instruments, US). A Tap150 probe (force constant 1.5 Nm⁻¹ to 15 Nm⁻¹, resonance frequency 175 kHz) from Budget Sensors (Bulgaria) was used to acquire the images, in air using tapping mode. As part of the image post-processing, the image background was flattened, while masking was used to preserve the features.

Samples for AFM were prepared on freshly-cleaved mica, which was exposed to a drop of diluted polymer solution (2 mgmL⁻¹) in water or potassium iodide solution (25 μM) and allowed to dry overnight.

3 Results and Discussion

3.1 Hofmeister Series Effect

It is known that ion-binding can change a grafted polymer's architecture from brush-to-globule which, in turn, can affect the polymers luminescent properties.^{36,40} We therefore decided to test the effect of anions from the Hofmeister series on the polycationic, PPV-g-PMETAC. Previously, the Hofmeister series has been shown to have induce significant effects on block-co-polymers bearing large sidechains.^{40,41} To ascertain the selectivity and sensitivity of binding with PPV-g-PMETAC, a range of potassium and sodium salts in water, from the Hofmeister series (Figure 2) were used.

The UV-Vis spectral data of the PPV-g-PMETAC solution (2 mgmL⁻¹) in water and solutions of various salts (25 μ M) are shown below (Figure 2a).

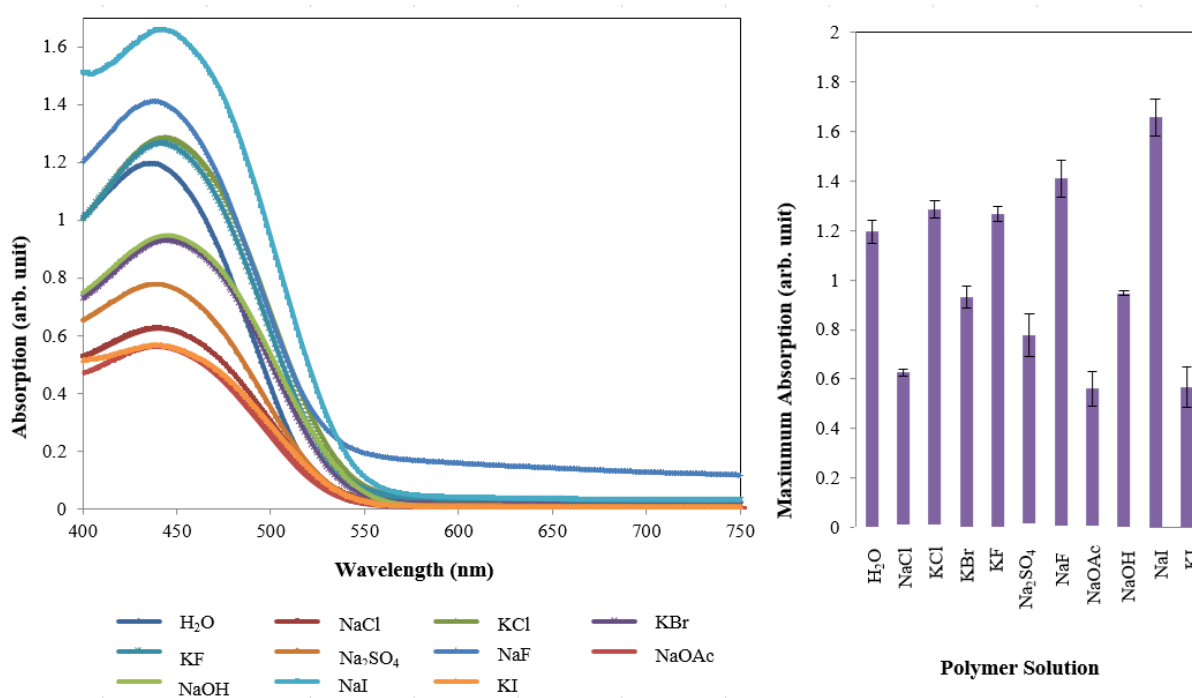


Figure 2. UV-Vis absorption spectra (left) and maximum absorption intensity (right) of PPV-g-PMETAC (2 mgmL⁻¹) in aqueous solutions (25 μ M) of salts.

The maximum absorption of PPV-g-PMETAC was observed at around 435 nm in water, which exhibited a spectral red shift when exposed to nearly every salt tested. The salts that showed the largest red-shift, measured to be nearly 10 nm, were the KBr, KCl, NaOH and NaI solutions.

Furthermore, it can also be noted that the absorption intensity decreased in all solutions except KF, KCl, NaF and NaI (Figure 2b). In order to ascertain any apparent relationship between the magnitude of the observed red shift and anion concentration, the UV-Vis of polymer solution (2 mgmL^{-1}) with various concentrations ($2.5\text{--}25 \text{ }\mu\text{M}$) of anion was analysed. These results, showed no obvious relationship between magnitude of the red shift and concentration of anion.

It is known that changes in molecular brushes, due to stimuli, transduce to neighbouring environments, in this case to the PPV backbone. To study this for PPV-g-PMETAC, the changes in intensity of fluorescence of polymer (2 mgmL^{-1} in water) and the Hofmeister salts ($25 \text{ }\mu\text{M}$) were measured (excitation wavelength = 435 nm , Figure 3a).

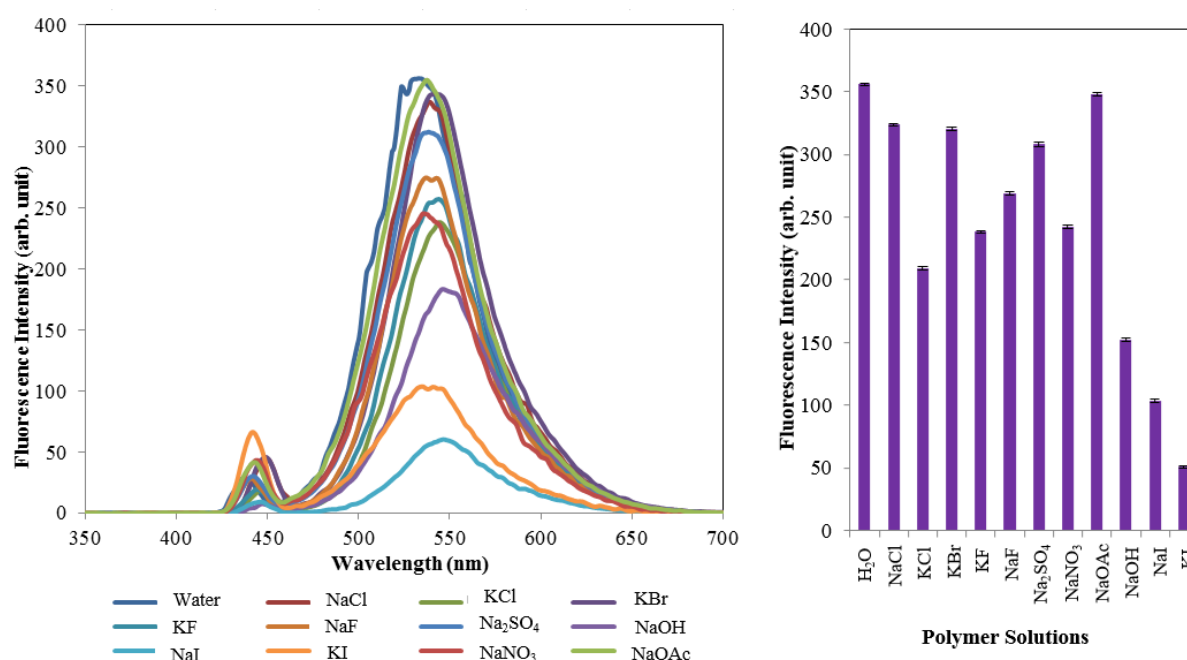


Figure 3. Fluorescence spectra (left) and fluorescent intensity at 535 nm (right), of PPV-g-PMETAC (2 mgmL^{-1}) in water containing various salts ($25 \text{ }\mu\text{M}$).

The maximum emission wavelength of PPV-g-PMETAC in water was found to be at $\sim 535 \text{ nm}$. In almost all cases, the fluorescent intensity at 535 nm of the polymer in salt solutions was reduced compared to that PPV-g-PMETAC in only water. This observed drop in fluorescent intensity was most prominent when the polymer was in the iodide salt solutions, compared to the other anions tested (Figure 3b). A 5 nm and 10 nm blue shift was seen for the polymer in the potassium iodide and sodium iodide solutions, respectively.

To additionally investigate how the photoluminescence properties of the grafted PPV is effected by the presence of iodide ions, the change in fluorescent intensity of the PPV-g-PMETAC when dissolved in NaI and KI solutions of various (2.5-25 μM) concentrations was also measured (Figure 4). The fluorescent intensity decreases with increasing iodide, in both NaI and KI solutions, with a four-fold decrease for KI when comparing 2.5 and 25 μM . When the other anions were tested at various concentrations a maximum of 10-25% decrease in fluorescence was observed at the highest concentration tested (25 μM) with the exception being for hydroxide where a 60% decrease was observed. The drop in fluorescence intensity was then measured for lower iodide concentrations, between $1 \times 10^{-6} \text{ molL}^{-1}$ and $6.5 \times 10^{-6} \text{ molL}^{-1}$ when KI was used as the iodide source (Figure S1).

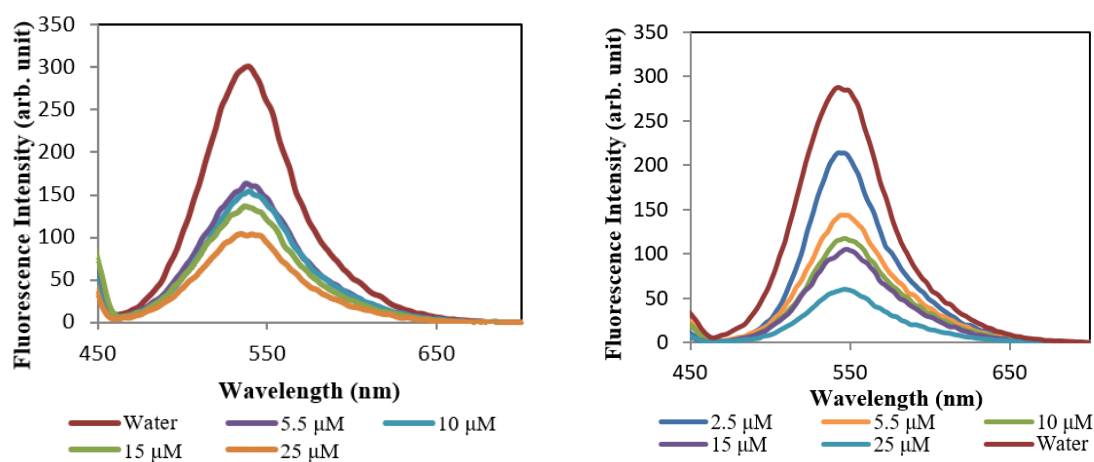


Figure 4. Effect of iodide concentration on fluorescent intensity of PPV-g-PMETAC using various concentrations of NaI (left) and KI (right).

It was found that the fluorescence intensity and iodide ion concentration had a negative, linear relationship ($R^2 = 0.98$). The detection limit (DL) was calculated, through extrapolation, to be approximately 10 nM, using the IUPAC equation where $DL = 3\sigma$, where σ is the standard deviation of the blank.⁴²

3.2 Determining the Effect of pH on Iodide Sensing

In order to assess the how pH effects the iodide sensing ability of PPV-g-PMETAC, the fluorescence intensity (at $\lambda_{Em} = 535 \text{ nm}$) of the grafted polymer (PPV-g-PMETAC in 25 μM KI) was recorded, while varying the pH from 2 to 14. The pH of PPV-g-PMETAC in pure water was measured to be 7.5. When the pH was reduced from 7.5 to 2 (using HCl), there was shown to be no significant changes in both the fluorescence intensity and spectral shift. This was not observed, however, when the pH was increased from 7.5 to 12 (using NaOH), which

resulted in a reduction of fluorescence intensity of approximately 32 %. When the pH was additionally increased from 12 to 14, a 10 nm red shift was observed, as well as a reduction in fluorescence intensity to ~46 % of the pH 7.5 value (Figure 5). It can be concluded that the wavelength of maximum fluorescence of PPV-g-PMETAC in the presence of iodide is not dependent on the pH when below 12. The useful range of pH for this system (2-12) is greater than previously reported sensors.²³⁻²⁵

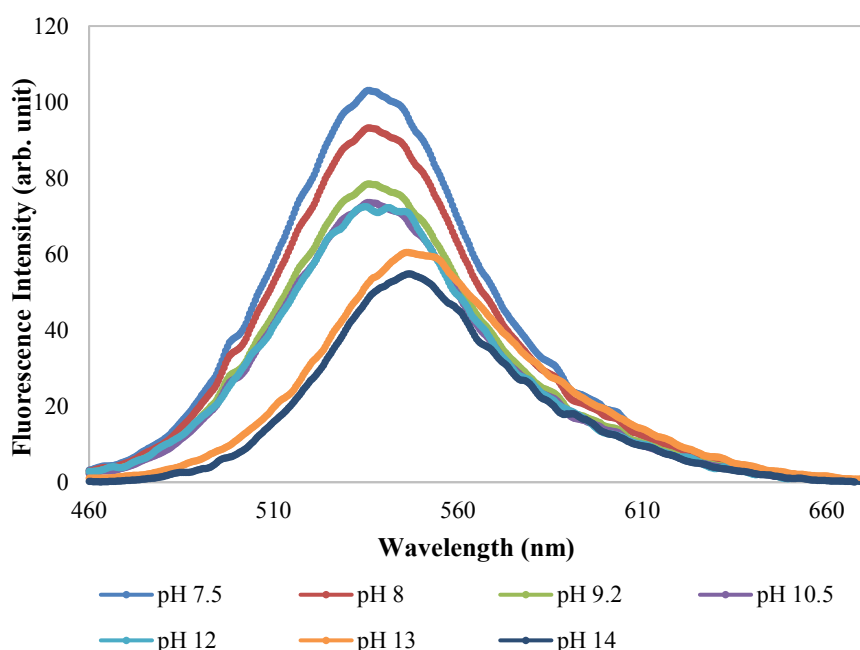


Figure 5. Fluorescence intensity of PPV-g-PMETAC in KI (25 μ M) at various pH \geq 7.5.

This pH-related behaviour of the polymer with iodide ions is also in accordance with that observed for the polymer with hydroxyl anions. Therefore, such a reduction in fluorescent intensity above pH 12 could be due to the synergic effect of high concentrations of iodide and hydroxyl ions, inducing additional quenching of fluorescence, along with a shift in the maximum emission wavelength.

3.3 Determining Temperature Effects

To determine what effect temperature has on spectroscopic properties and the ion-sensing ability of PPV-g-PMETAC, the fluorescence intensity at 535 nm was measured whilst changing the temperature (25-70 $^{\circ}$ C), using a solution of PPV-g-PMETAC (40 μ g mL⁻¹ in water), (Figure S2). The fluorescent spectrum, with increasing temperature, showed only a

small reduction in fluorescence intensity and no notable shifting of the maximum emission wavelength. The fluorescent intensity decreased roughly linearly with increasing temperature.

A further experiment was also conducted measuring the emission at 535 nm using the polymer ($40\ \mu\text{g mL}^{-1}$) in $25\ \mu\text{M}$ KI solution (Figure S3). Analysis of the results indicate a negative, non-linear relationship exists between temperature and the relative fluorescence intensity. When the temperature increases, the turbidity of the solution would vary, resulting in the random movement of iodide ions in the solution, which could account for the observed non-linearity of the relationship.

3.4 Reversibility of Iodide Binding

When conducting these experiments it was noticed that the colour of highly concentrated PPV-g-PMETAC-anion solutions were yellow for all anions except iodide which were orange-red in colour. To visually determine if the observed iodide-induced quenching of PPV-g-PMETAC was reversible through displacement of the bound iodide ions, a solution of $2.5\ \text{M}$ KCl was added to a sample of polymer dissolved in KI solution. It could be seen that the solution underwent a colour change (orange-red, which became yellow) when chloride anions were added.

To quantitatively determine this reversibility, the change in intensity of fluorescence at 535 nm was recorded, when solutions of polymer ($0.1\ \text{mg mL}^{-1}$ in $2.5\ \mu\text{M}$ KI) were treated with KCl solutions of various concentration. As expected, the intensity of fluorescence of the grafted polymer solution increased when the concentration of KCl increased (Figure 6) showing the reversibility of the binding of iodide to PPV-g-PMETAC.

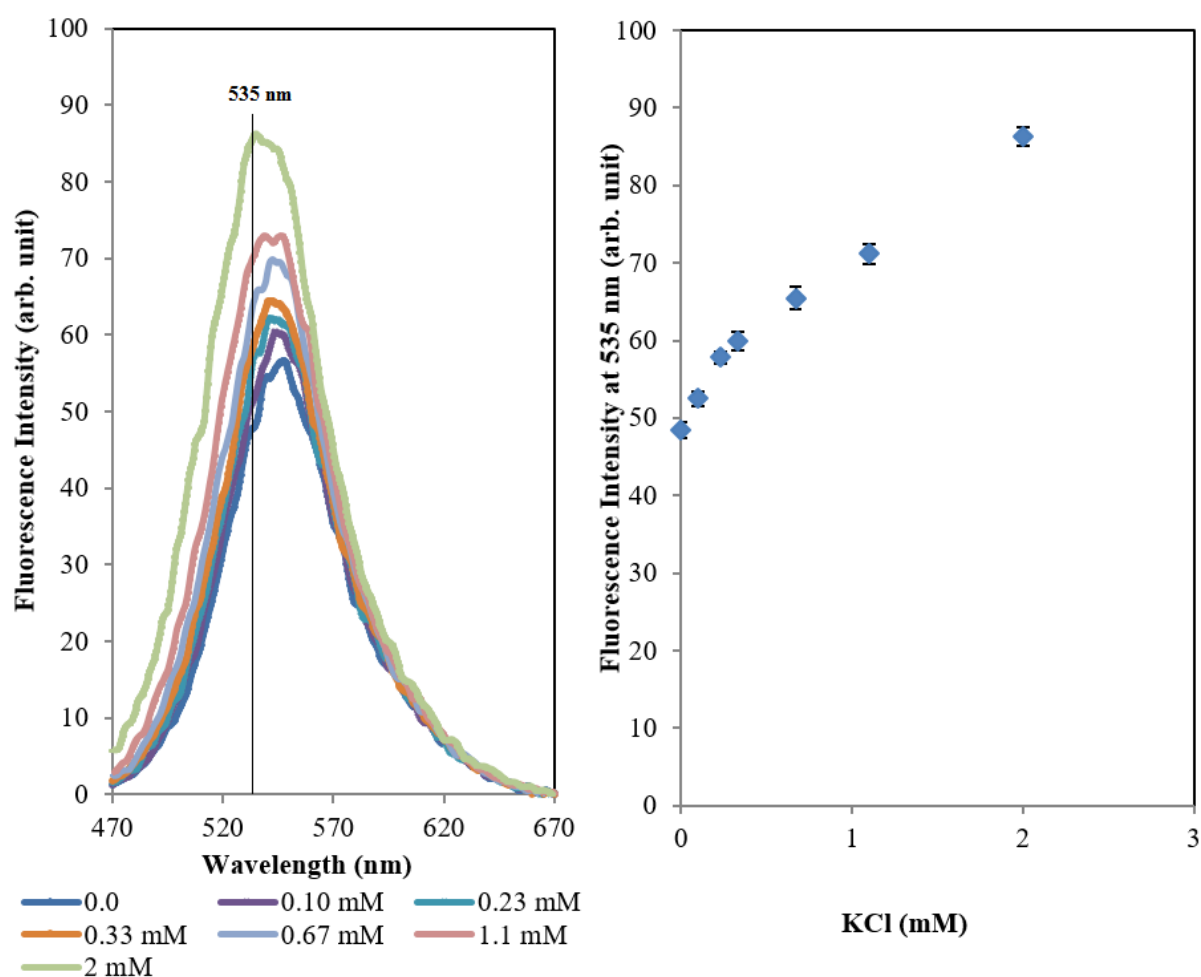


Figure 6. Change of fluorescence intensity of PPV-g-PMETAC in 2.5 M KI solution upon addition of KCl.

3.5 Iodide Sensing Mechanism

The changes in fluorescence intensity when exposed to iodide ions can be explained by considering the effect of changes in morphology of the grafted brushes on the CP backbone when the native chloride counter-ions are displaced by other anions. Iodide ions are known to be potent chaotropic agents, disrupting the hydrogen-bonding network of macromolecules in water.⁴³

While water is an ideal solvent for the highly charged PMETAC polymer brushes found in PPV-g-PMETAC, for the lipophilic PPV backbone it is a poor solvent. Previous studies^{36,44-46} have shown that there exists steric interactions between the water-soluble grafted molecular brushes and the lipophilic backbones which prevents multimolecular polymer aggregation, resulting in water soluble grafted co-polymers, commonly with a micellar structure. Because

of this, it was hypothesised that PPV-g-PMETAC, with its densely packed, long length, positively-charged quaternary ammonium brushes, would also exhibit a micellar structure when placed in water.

Iodide is a strong chaotrope, which, if added, can disrupt these intramolecular interactions of PPV-g-PMETAC, inducing a “salting out” process resulting in collapsing of the grafted molecular brushes, which could subsequently reduce intermolecular interactions due to a decrease in charge repulsion.

To investigate these effects and monitor the structural changes of PPV-g-PMETAC when exposed to iodide ions, dynamic light scattering (DLS) and atomic force microscopy (AFM) were performed. AFM (tapping mode) was utilised to observe the PPV-g-PMETAC in water (Figure 7; A and C) and iodide solution (25 μM , Figure 7; B and D). As can be seen, there was a notable difference in conformation of the polymer in these two different media. Large aggregates were observed when PPV-g-PMETAC was deposited in an iodide solution, whereas these aggregates were not present for the polymer deposited from water.

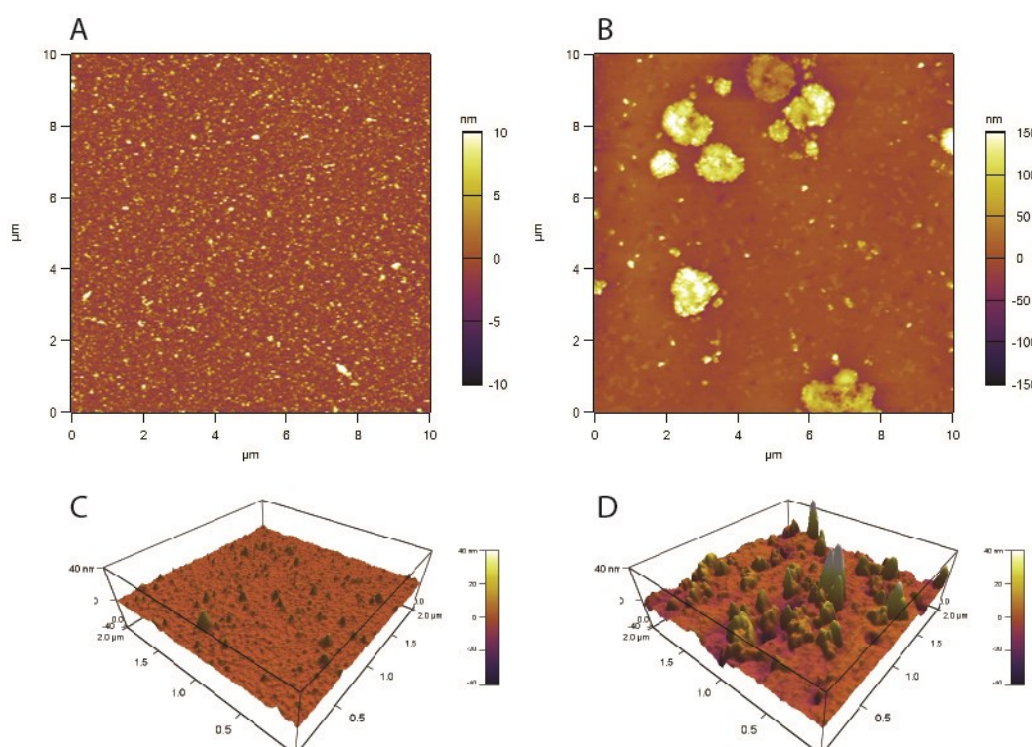


Figure 7. AFM images of PPV-g-PMETAC in water (A, C) and iodide solution (B, D). Scan size 10 μm in A and B, and 2 μm in C and D. The vertical scale is 20 nm in A, 300 nm in B and 80 nm in C and D.

Furthermore, DLS was used to analyse the size distribution of PPV-g-PMETAC in both water and iodide solutions at various concentrations (Figure 8).

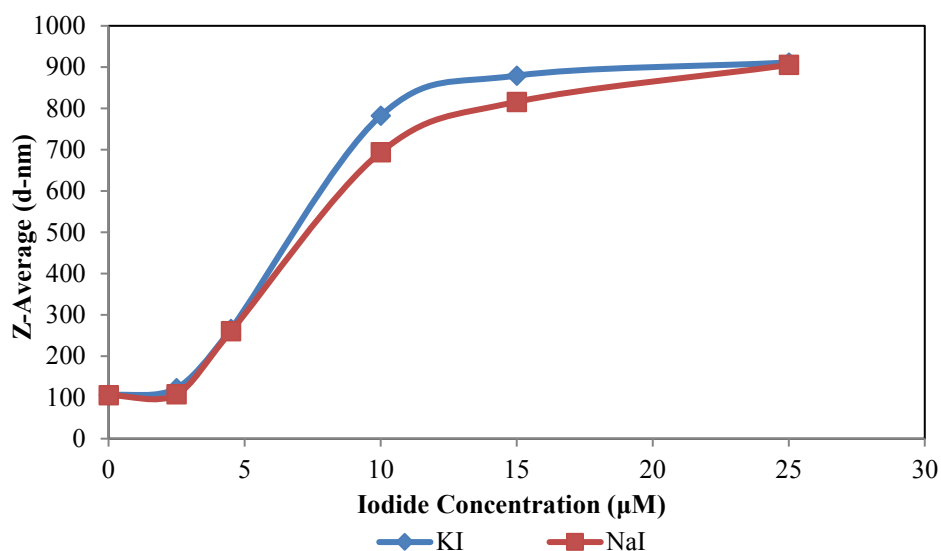


Figure 8. DLS measurements of average size diameter changes of PPV-g-PMETAC in KI and NaI solutions of different concentrations.

It was observed that increasing the iodide ion concentration from 0 to 25 μM for both KI and NaI, results in an increase in average polymer size from ~ 120 nm to ~ 900 nm. These DLS results concur to those found in AFM studies.

4 Conclusions

In conclusion, we report that PPV-g-PMETAC is a selective and sensitive chemical sensor for iodide ions in solution. The obtained results reveal that PPV-g-PMETAC affords good selectivity for iodide ions. Through changes in fluorescence intensity, it could be determined that PPV-g-PMETAC has a 10 nM detection limit for iodide ion sensitivity. This detection level is comparable or better than other chemical fluorescent²¹⁻²⁵ iodide sensors but does not rely on the use of toxic mercury salts,^{23,25} which are commonly found in the most sensitive materials. Furthermore, the useful pH range is greater than previously reported iodide sensors.

The sensing mechanism for iodide was studied using AFM and DLS experiments, with results indicating that grafted molecular brushes aggregate in the presence of iodide ions, which modifies polymer fluorescence. Factors such as pH and temperature do not notably affect the iodide sensing ability of the grafted polymer and the fluorescence quenching effect of iodide is reversible upon exposure to chloride ions.

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